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**FREE PRODUCT VOLUME ANALYSIS  
L.E. CARPENTER AND COMPANY  
WHARTON, NEW JERSEY  
SRP NO. NJD002168748**

**PREPARED BY RMT, INC.  
ON BEHALF OF  
L.E. CARPENTER AND COMPANY**

May 2000

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# Executive Summary

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The volume of free product at the L.E. Carpenter site in Wharton, New Jersey, has been estimated using an empirical relationship between the "true" and apparent thickness of LNAPL (light nonaqueous-phase liquid) measured in on-site monitoring wells. Apparent free product measurements from 32 monitoring wells and EFR (enhanced fluid recovery) wells were analyzed using an Excel spreadsheet model developed by the American Petroleum Institute (API), to calculate "true thickness" values at each of the well locations. "True" LNAPL thickness values were plotted on a map of the site, and the volume of LNAPL was then calculated using a volume estimation model.

The results of the API model analysis indicate that the total volume of LNAPL at the site is approximately 44,000 gallons. The free product is present in variably-saturated soil pores in a "smear zone," caused by seasonal water table fluctuations. Due to its viscosity and partial saturation in the soil, there is considerable resistance to flow, making much of the free product unavailable for recovery. Of the total volume of free product, 20 to 30 percent, or 8,800 to 13,000 gallons, is estimated to be recoverable based on experience at similar sites (USEPA, 1996; Testa and Paczkowski, 1989).

An alternative method of estimating the recoverable volume of LNAPL at the site is through extrapolation of the cumulative free product recovery versus time curve (USEPA, 1996). If the historical, cumulative free product recovery curve is projected logarithmically into the future, it is estimated that approximately 8,000 gallons of free product are recoverable at the site.

Thus, two methods of calculating the volume of recoverable free product at the site indicate that between 8,000 and 8,800 to 13,000 gallons of free product are recoverable. The 8,000-gallon estimate of recoverable free product may be the best estimate, because it is based on actual results of free product recovery (USEPA, 1996), and takes into account the limitations of recoverability caused by the viscous nature of the free product and the low hydraulic conductivity caused by variable saturation with free product in the "smear zone."

If the volume of recoverable free product at the site is 8,000 to 13,000 gallons, then, at the present rates of recovery of approximately 50 gallons per month, it would take approximately 13 to 22 years to remove all of the recoverable volume using the current EFR methodology. However, given the inherent uncertainties in the calculations, estimates of cleanup time should be viewed as order of magnitude estimates (EPA, 1996; Testa and Paczkowski, 1989).

# Section 1

## Introduction

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"Free product" is present at the L. E. Carpenter site at a number of monitoring wells in the form of floating LNAPL (light nonaqueous-phase liquid). The extent of free product at the site, shown on Figure 1, covers an area of approximately 100 feet by 600 feet. Apparent product thickness values in monitoring wells and EFR (enhanced fluid recovery) wells typically have been less than a foot, but have ranged up to approximately 9 feet, over the past few years. Free product recovery has occurred since 1997, using EFR methods to remove free product from a system of 28 EFR wells. Since EFR recovery began in November 1997, approximately 2,000 gallons of free product have been removed (RMT, 1999).

The New Jersey Department of Environmental Protection requested in a letter dated August 17, 1999, that a volumetric estimate of the volume of free product at the site be conducted, and that the time to recover the free product also be estimated. To help measure progress toward remediation of the free product area, a detailed analysis of the existing volume of free product has been conducted. This information will be important in evaluating the effectiveness of current approaches at removing free product at the site, and in estimating the time needed to remove recoverable free product. The results of that analysis are presented here.

## Section 2

# Site Hydrogeologic Conditions

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The hydrogeologic conditions of the site have been presented in the 1990 Report of Revised Investigation Findings, L.E. Carpenter & Company, by GeoEngineering, Inc., and in the 1992 Weston report entitled Final Supplemental Remedial Investigation Addendum for L.E. Carpenter and Company. The reports describe an upper unit of low-permeability alluvial silt and clay, and fill of similar texture, that occurs at depths of less than 30 feet. More recent borings at the site indicate that the upper 10 to 15 feet of soil are composed of poorly-sorted gravelly silty sand and sandy silt and clay with boulders. An injection test and an infiltration test conducted in the shallow silt and clay unit indicate that the unit is much lower in permeability than the deeper units of outwash and stratified drift (Weston, 1996). The deeper, permeable units are up to 170 feet total in thickness and are generally composed of sand and gravel.

Free product occurs in the upper 15 feet of formation at the site, and in most cases, is within 5 to 10 feet of the surface. At some locations, the free product occurs within poorly-sorted gravelly, silty sand, whereas at other locations it occurs within sandy silt and clay. Boring logs from each of the wells where free product was measured were reviewed to determine in which soil type the free product occurred.

Shallow groundwater flow is substantially affected by adjacent surface water bodies. Groundwater is recharged from the Rockaway River, and discharges into the drainage ditch that lies to the north and east of the free product zone. In general, the shallow groundwater flows to the north and east, toward the drainage ditch that borders the site. Vertical gradients are upward toward the shallow groundwater zone.

## Section 3

# Previous Analyses

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An earlier estimate of the volume of free product at the site was previously presented by Weston (1997). Using the free product baildown test methods that are documented in Gruszinski (1987), Weston analyzed results from six monitoring wells, and estimated that approximately 30,000 gallons of free product existed in the aquifer on-site. Only a fraction of the total volume of free product in the formation is recoverable, due to the specific retention of the aquifer for the free product, and the inability of the free product to migrate through small pores. Using assumed recoverability values of 5 percent to 20 percent of the total volume of free product, Weston calculated that approximately 1,500 to 5,900 gallons of the free product were recoverable.

Weston's estimate of free product was based on an assumed aquifer porosity of only 20 percent, whereas Carsell and Parish (1988) cite average porosity values ranging from 38 to 46 percent for clay, silt, and sand. Also, Weston assumed that only 5 to 20 percent of the free product was recoverable, whereas the USEPA (1996) reports that the recoverability of gasoline and other low-viscosity hydrocarbons at actual sites typically ranges from 20 to 50 percent, and Testa and Paczkowski (1989) report that recoverability is typically 20 to 30 percent of the pore volume for fine sand. Testa and Paczkowski (1989) acknowledge that recoverability of hydrocarbons in lower permeability soil can be significantly lower. Furthermore, more viscous fluids, such as DEHP, have more resistance to flow, which tends to lower the recoverability. Overall, Weston's assumed lower porosity values and lower recoverability values likely underestimated the amount of free product and recoverable free product that actually exists at the site.

## Section 4

# Theoretical Background and Methods

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Revised estimates of the volume of free product that exists in the subsurface at the site have been conducted using an empirical relationship between apparent LNAPL thickness in a monitoring well and the volume of NAPL per unit area of the aquifer formation. In the recent publication by the American Petroleum Institute, Free-Product Recovery of Petroleum Hydrocarbon Liquids (Charbeneau et al., 1999), methods for calculating the volume of free product in the formation are presented. The free-product volume calculations involve soil physical properties, as well as physical properties for the free product. The distribution of free product in the soil may be determined from monitoring well free product measurements, and from the water retention curve for the soil; this assumes there is hydrostatic equilibrium between the fluids in the well and those in the formation. The soil and free product parameters are used to estimate the "true thickness" of free product in the formation based on the apparent thickness of product in wells. An Excel spreadsheet is available with the API publication (Charbeneau et al., 1999) that facilitates the solution of the equations.

The "true thickness" of free product is best thought of as a volume of free product per unit area of formation. For convenience, the term "true thickness" will be used in this report, to mean an equivalent thickness of free product equal to the volume of free product per unit area. It is understood that the free product exists in the aquifer not as a distinct layer of 100 percent LNAPL, but as a zone in which the soil pores are variably saturated with LNAPL, up to 100 percent. This conceptual model is illustrated on Figure 2.

The API spreadsheet model offers two options for analysis of "true thickness" of free product, both of which relate soil properties to "true" free product thickness: the Brooks-Corey method, and the van Genuchten method. The van Genuchten (1980) method of analyzing the "true thickness" of free product was the option used in this report, because of its ability to more accurately calculate free product thickness for thin layers of NAPL.

Important soil variables (which vary with soil texture) that are used in the calculations of LNAPL volume include soil porosity, displacement pressure head, and residual NAPL saturation. Carsell and Parish (1988) have conducted a statistical evaluation of physical parameters for a large number of soil samples of varying texture from across the U.S., and have tabulated the mean values for these physical parameters for soil types of different texture. As appropriate, depending on the type of soil that the free product occurred in, site-specific values of these soil parameters were assigned at each location analyzed, using table values for specific

soil textures, from Charbeneau et al. (1999). Soil texture information was gathered from boring log descriptions for each well location, and from grain-size analyses where available.

Free product parameters that are important in the calculations include viscosity, density, NAPL/water interfacial tension, and air/NAPL surface tension. Because of the sensitivity of the model results to the NAPL characteristics (V. Kremmesec and R. Kolhatkar, Amoco Corporation, personal communication, 1999), three samples of free product and groundwater were collected for determination of site-specific values of viscosity, density, NAPL-water surface tension, and air-NAPL surface tension.

Free product thicknesses from site monitoring wells and EFR wells have been measured monthly since November 1997. Measurements from April 1999 were used to calculate the volume of free product that exists in the formation. The free product thickness totals from all monitoring wells were similar in April, May, and June of 1999, and therefore the April values are considered representative of conditions during the second quarter of 1999.

Site-specific soil and LNAPL physical parameters and free product measurements were analyzed using the API Excel spreadsheet model, which calculates "true thickness" of free product from monitoring well measurements (Charbeneau et al., 1999). The "true thickness" values of free product were plotted on a map of the site, and were used to calculate the volume of NAPL, using the Siteworks volume calculation program contained in Intergraph. A triangulation method was used to interpolate between known points in the volume calculations.



# Section 5

## Findings and Conclusions

### LNAPL Physical Characteristics

Site-specific data on the physical properties of the free product were collected to help define these important variables with more certainty. LNAPL and water samples were collected from wells MW1R, EFR11, and WP A8, to provide representative samples from three portions of the site. The three samples were collected in October 1999, and shipped to Saybolt Labs of Pasadena, Texas, for analysis. The values of these parameters are presented in Table 1.

Table 1  
Site-specific LNAPL Physical Properties

Well Sample	Density	Interfacial Tension (dynes/cm)	Surface Tension (dynes/cm)	Viscosity (cSt)
MW1R	0.9066	12	21	2.013
EFR11	0.9479	14	28	6.983
WP A8	0.9545	15	23	10.33

Based on an evaluation of these values relative to the site locations, two zones were delineated for assignment of NAPL parameter values: a western zone (western quarter of the free product area) with NAPL characteristics of MW1R; and an eastern zone (eastern three-quarters of the free product area), with NAPL characteristics that were the mean of the values from EFR11 and WPA8. Table 2 presents the values assigned to the two zones.

Table 2  
Assigned LNAPL Physical Properties Zones

	Density	Interfacial Tension (dynes/cm)	Surface Tension (dynes/cm)	Viscosity (cSt)
Zone 1	0.91	12	21	2.013
Zone 2	0.95	14.5	25.5	8.5

### LNAPL "True Thickness" Calculations

Product thickness measurements at 32 EFR and monitoring well locations (wherever measurable product thickness was found and a boring log was available) were analyzed using the API's Excel spreadsheet model for calculating NAPL volume per unit area ("true

thickness")(Charbeneau et al., 1999). Model output from the API free product model is presented in Appendix A.

Table 3 presents values of measured free product thickness and "true thickness" at each of the 32 points at the site where free product was measured in April 1999. "True thickness" values ranged from 0 feet to 1.5 feet across the free product zone. The distribution of the "true" LNAPL thickness is shown on Figure 2. From this figure, it is clear that the "true thickness" values vary widely from point to point across the free product area.

## **LNAPL Volume Calculations**

Once the "true thickness" values of free product were obtained at individual well locations using the API model, the volume over the entire free product area was calculated. A volume calculation program in Intergraph called Siteworks (Intergraph, 1993) was used to calculate the free product volume, using the 32 values of "true thickness," as well as 36 zero values where product was not found. Triangulation between known values was used in the volume calculation routine to estimate the total volume of free product. The volume calculation results are presented in Appendix B.

The calculated volume of free product in the formation at the site is approximately 44,000 gallons. This value is more than the 30,000-gallon reported volume of total free product cited by Weston (1997), but is less than a 60,000-gallon corrected estimate of free product using Weston's baildown test methods, if a more representative porosity value of 40 percent is used in their analysis. The current estimate of 44,000 gallons of free product was developed using a total of 68 monitoring well/EFR well locations, compared with only 6 by Weston. However, all methods of estimating free product volume have significant uncertainty associated with them, and the estimate of free product volume may only be accurate to within +50 percent to +100 percent, as noted by the USEPA (1996).

Sensitivity testing was conducted to evaluate the effect of having the free product occur in a loam soil (composed of significant sand, silt, and clay) instead of a sandy loam or loamy sand, as most of the well logs indicate for the free product zone. The data from all of the EFR wells were revised to simulate a loam soil zone instead of a loamy sand zone where the free product occurs. The results indicate that the calculated free product would not change significantly if the free product at those wells occurred in loam instead of loamy sand.

## **LNAPL Recoverable Volume**

Of the 44,000 gallons of free product calculated for the site, only a portion is recoverable, due to constraints of the formation permeability to the flow of free product. As discussed above, experience at actual remediation sites has shown that, typically, only about 20 to 30 percent of

the total free product volume at a site is recoverable (Testa and Paczkowski, 1989). Of the 44,000 gallons of free product estimated for the site, the 20 to 30 percent recovery range corresponds to 8,800 to 13,000 gallons of recoverable product. However, as noted by Testa and Paczkowski (1989), the amount of recoverable free product decreases in finer sediment, and decreases with more viscous fluids, and therefore, may be at the lower end of this range.

**Table 3**  
**Measured Free Product Thickness Versus "True Thickness"**

WELL ID	MEASURED THICKNESS (ft)	"TRUE THICKNESS" (van Gennuchten method) (ft)
EFR-1	1.13	0.34
EFR-2	1.46	0.46
EFR-3	0.36	0.06
EFR-4	0.08	0.01
EFR-5	2.65	0.72
EFR-6	0.61	0.08
EFR-7	0.07	0.01
EFR-8	0.03	0.01
EFR-9	0.11	0.01
EFR-10	4.97	1.52
EFR-11	2.02	0.51
EFR-12	0.02	0.004
EFR-13	0.49	0.06
EFR-15	0.01	—
EFR-17	0.06	0.01
EFR-18	0.06	0.003
EFR-19	0.44	0.05
EFR-20	0.43	0.09
EFR-21	2035	0.78
EFR-22	0.95	0.17
EFR-23	0.22	0.02
EFR-25	1.08	0.21
EFR-26	0.75	0.12
EFR-28	1.65	0.53
MW-1R	0.34	0.06
MW-3	1.02	0.13

**Table 3 (continued)**  
**Measured Free Product Thickness Versus "True Thickness"**

WELL ID	MEASURED THICKNESS (ft)	"TRUE THICKNESS" (van Genuchten method) (ft)
MW-11S	5.93	0.89
RW-1	0.50	0.13
WP-A6	3.50	1.20
WP-A7	0.59	0.08
WP-A9	0.55	0.07
WP-B1	0.04	0.02
WP-B5	0.88	0.15

Note: Wells that contained no measurable free product in April 1999 are not listed in this table.

## **LNAPL Recoverable Volume Estimates Based on Extrapolation of Recovery Versus Time**

Recovery of free product at the site using EFR methods has collected over 2,000 gallons of free product, from November 1997 to the present. The amount of free product recovered per EFR event has decreased over time, from an initial value of over 300 gallons, to approximately 50 gallons per event in recent months.

Free product recovery typically decreases logarithmically over time (USEPA, 1996). As free product is removed and the thickness decreases, the ability to recover free product becomes more difficult. The permeability of the soil to NAPL decreases substantially as the degree of saturation of the formation with respect to free product decreases (see Figure 3). Eventually, as the product thickness becomes very small and the percent saturation with respect to free product decreases, the permeability of the formation for free product decreases to such small values that it no longer flows into recovery wells. The free product then becomes immobile and recovery ceases.

USEPA guidance on evaluating the effectiveness of free product recovery measures indicates that extrapolation of cumulative recovery totals may offer a reasonable estimate of total recoverable free product at a site (USEPA, 1996). Figure 4 shows the pattern of cumulative free product recovery over time at the site. As shown on Figure 4, extrapolation of cumulative free product recovery values indicates that there may be only approximately 8,000 gallons of free product that are actually recoverable at the site.

## **Comparison of LNAPL Volumes Calculated by Different Methods**

In conclusion, revised methods of calculating the volume of free product based on 68 monitoring well measurements indicate that up to approximately 74,000 gallons of free product are present. Of this amount, it is estimated that up to 15,000 to 22,000 gallons of free product are recoverable. However, using EFR performance results from the site, extrapolation of free product recovery data indicates that only approximately 8,000 gallons of free product may be recoverable.

The apparent discrepancy between the two volume estimates is caused by the resistance of the free product to flow, which impedes recovery efforts and in turn lowers the estimate of recoverable free product, relative to the total volume of free product. Observations in the field during recovery efforts show that, once the free product in a well is removed, it requires several days to return to a similar level. As illustrated on Figure 2, the pores in the soil are only partially saturated with free product; the hydraulic conductivity of the soil to free product is substantially reduced when the free product occupies only a fraction of the pore space. The

high viscosity of the free product, coupled with low hydraulic conductivity of the soil to free product, results in substantial resistance to flow to a well. This resistance to flow results in a relatively small amount of the product that is able to be recovered from EFR wells.

In summary, it is estimated that approximately 8,000 gallons of free product are recoverable based on extrapolation of EFR recovery data. The total volume of free product in the aquifer is estimated at 44,000 gallons. Much of this is likely smeared over 5 vertical feet of aquifer as the free product rises and falls with the water table; it does not occur as a discrete layer in the aquifer, of pure free product (see Figure 2). Because the bulk of the estimated 44,000 gallons of free product occurs in variably saturated pore spaces between soil particles, it has relatively high resistance to flow, resulting in relatively low estimates of recoverable free product, ranging from 8,000 gallons (based on EFR recovery data) to 8,800 to 13,000 gallons (based on literature values for typical percent recoverability).

## Section 6

# References

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\$\$\$PRF\$\$\$  
\$\$\$PTABLE\$\$\$

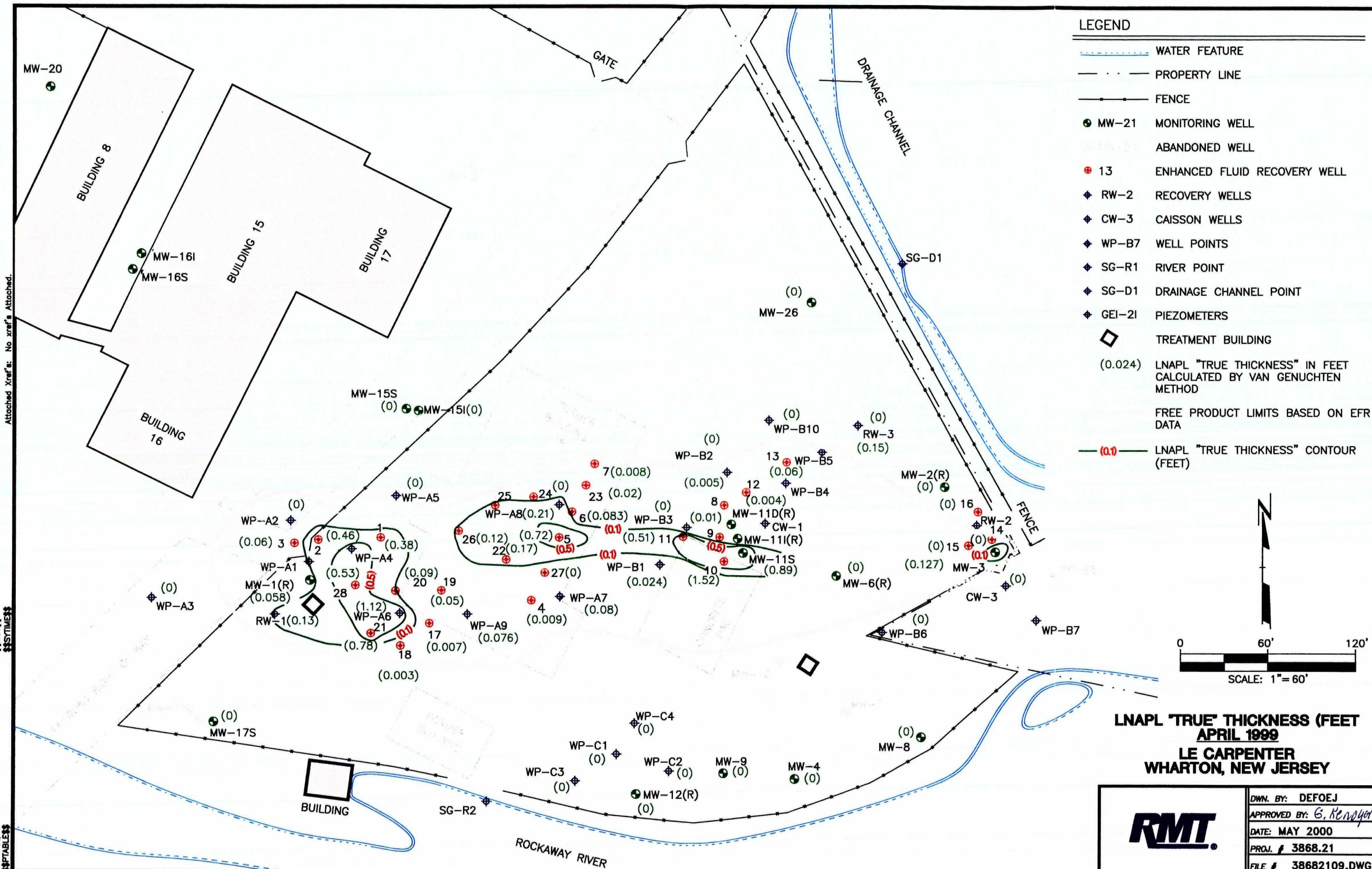


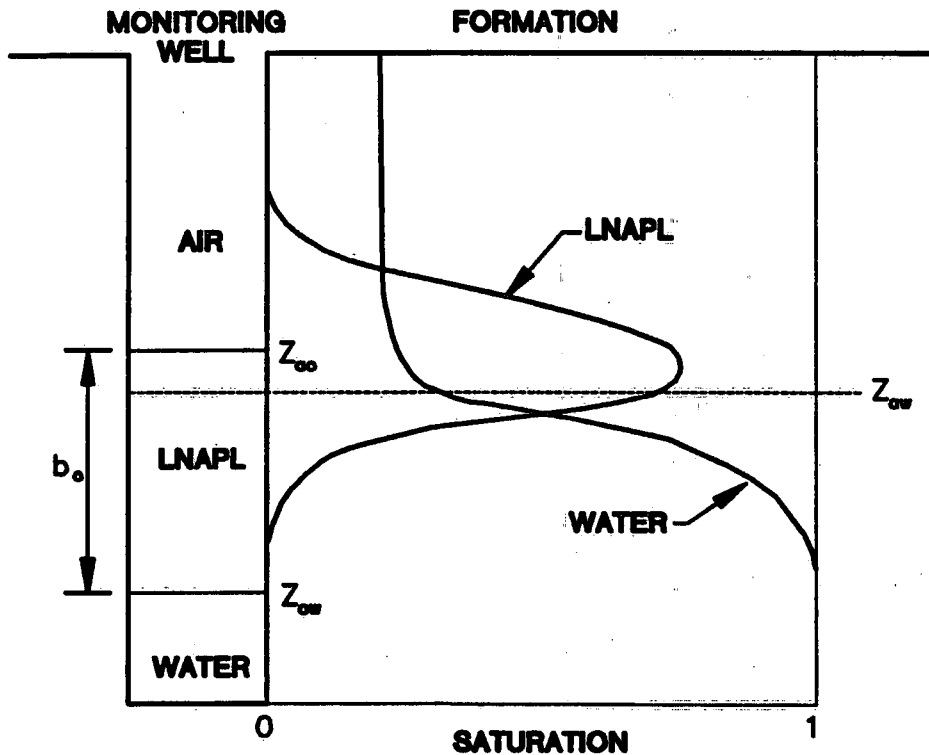
FIGURE 1

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**FIGURE 2** LNAPL/WATER DISTRIBUTION WITHIN THE FORMATION AND IN A MONITORING WELL FOR FLOATING FREE-PRODUCT HYDROCARBON

**RMT.**

DWN. BY: BREWSTEK  
APPROVED BY: *G. Kenoyer*  
DATE: MAY 2000  
PROJ. # 3868.21  
FILE # 38682101.DWG

**FIGURE 2**

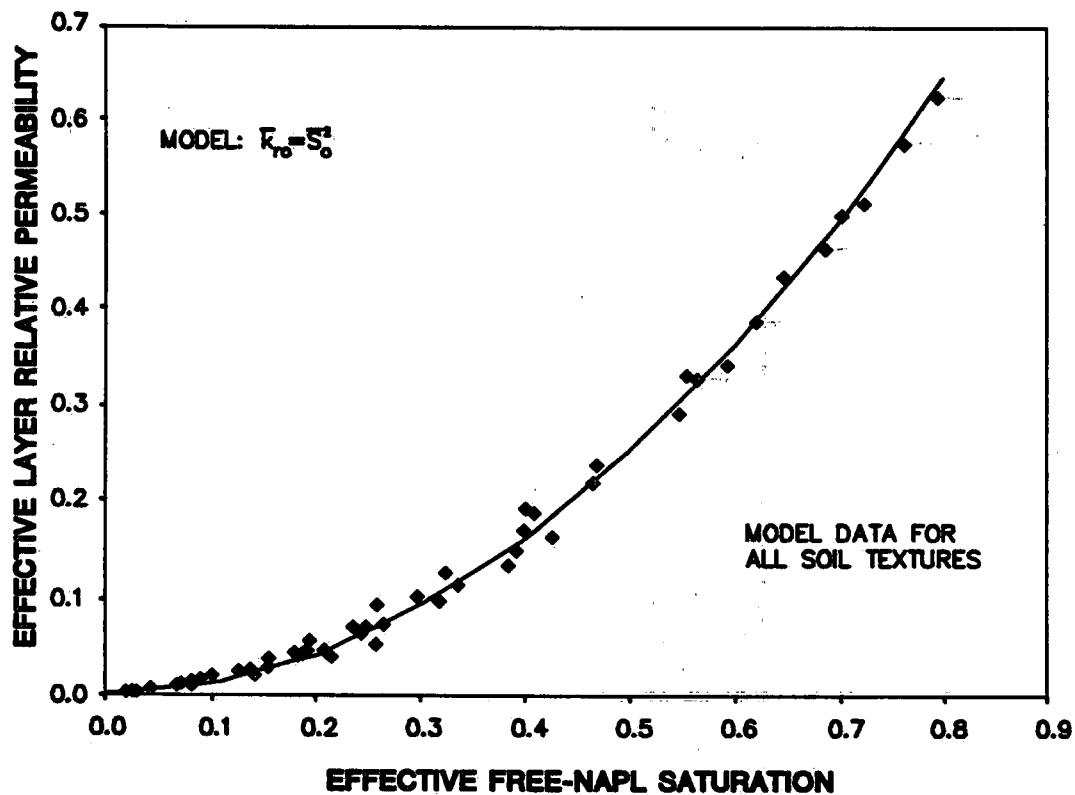


FIGURE 3 EFFECTIVE LNAPL LAYER RELATIVE PERMEABILITY

FIGURE IS ADOPTED FROM CHARBENEAU ET AL. 1999

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**RMT.**

DWN. BY: BREWSTEK
APPROVED BY: <i>G. Kinyer</i>
DATE: MAY 2000
PROJ. # 3868.21
FILE # 38682102.DWG

FIGURE 3



## Cumulative Free Product Recovery (gallons)

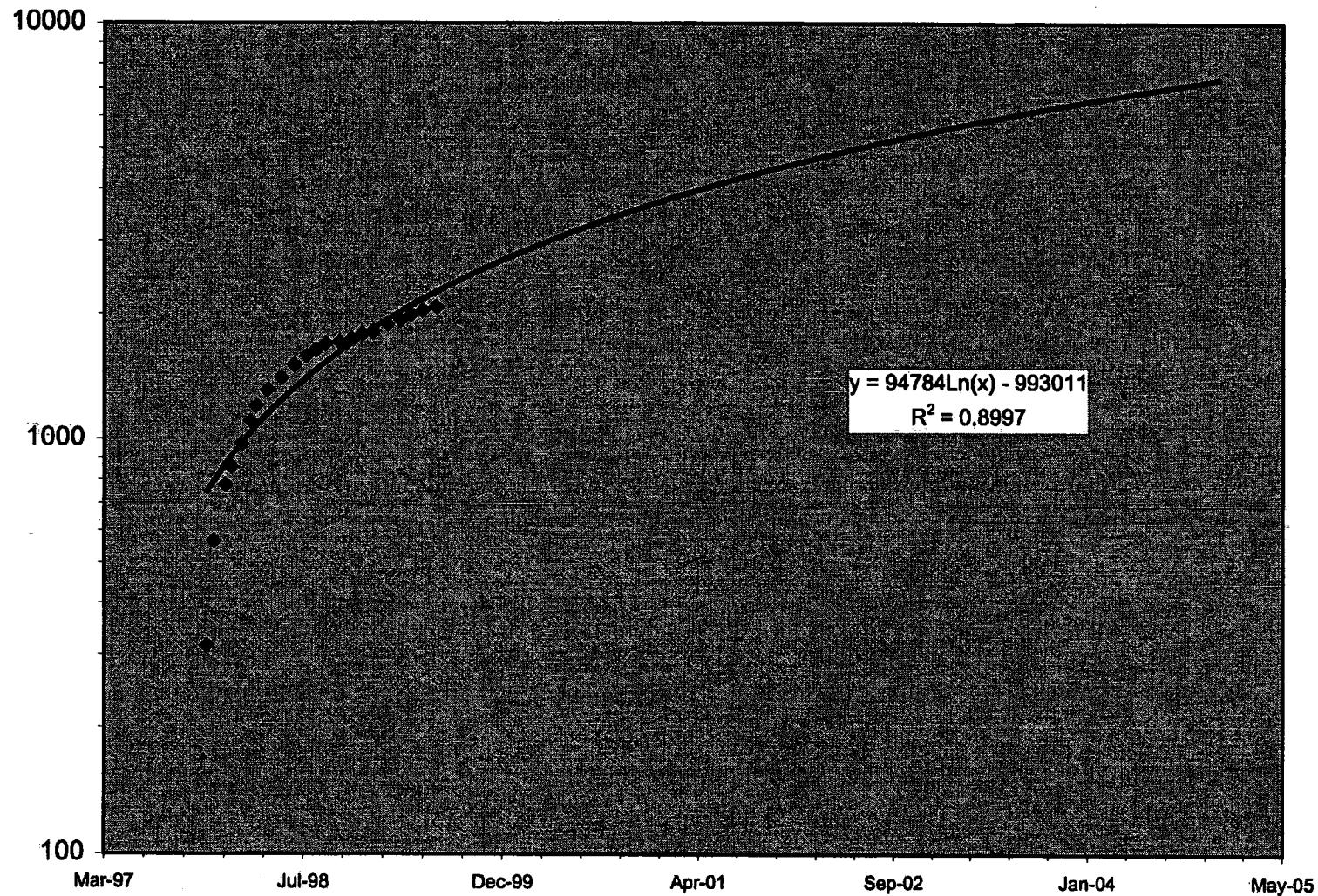


Figure 4  
Cumulative Free Product Recovery

# Appendix A

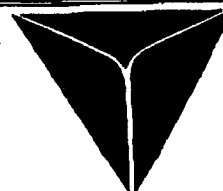
## Laboratory Data Sheets, LNAPL Analysis, Physical Parameters

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**SAYBOLT INC.**  
Petrochemical Division  
3113 Red Bluff Road  
Pasadena, Texas 77503  
Phone: (713) 230-0515  
FAX: (713) 230-0537

**CERTIFICATE OF ANALYSIS**

**Job Number: L9910.222A**



**SAYBOLT**

**PRODUCT:** Unknown  
**SAMPLE MARKED:** Oil MW-1R  
**SUBMITTED BY:** RMT Inc., Chicago, Illinois  
**RECEIPT DATE:** October 23, 1999  
**ANALYSIS DATE:** October 25, 1999


**RESULTS OF ANALYSIS:**

**UNITS**

**TEST RESULTS**

**METHODS**

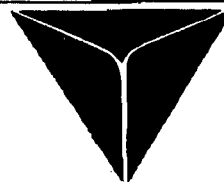
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Interfacial Tension	dynes/cm	12	ASTM D-971
Viscosity @ 100°F	cSt	2.013	ASTM D-445
API Gravity @ 60°F		0.9066	ASTM D-4052

  
Representative of Saybolt Inc.  
Pasadena, Texas

SAYBOLT INC.  
Petrochemical Division  
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Pasadena, Texas 77503  
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FAX: (713) 230-0537

**CERTIFICATE OF ANALYSIS**

Job Number: L9910.222A



**SAYBOLT**

**PRODUCT:** Unknown  
**SAMPLE MARKED:** ~~01 EFR~~ EFR-11\*  
**SUBMITTED BY:** RMT Inc., Chicago, Illinois  
**RECEIPT DATE:** October 23, 1999  
**ANALYSIS DATE:** October 25, 1999

**RESULTS OF ANALYSIS:**

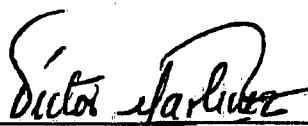
**UNITS**

**TEST RESULTS**

**METHODS**

Surface Tension	dynes/cm	28	ASTM D-1331A
Interfacial Tension	dynes/cm	14	ASTM D-971
Viscosity @ 100°F	cSt	6.983	ASTM D-445
API Gravity @ 60°F		0.9479	ASTM D-4052

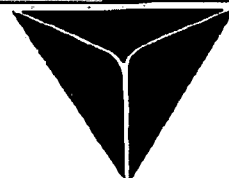
\* Sample name was corrected based on information from Nick Clevert, RMT.

  
Representative of Saybolt Inc.  
Pasadena, Texas

**SAYBOLT INC.**  
**Petrochemical Division**  
**3113 Red Bluff Road**  
**Pasadena, Texas 77503**  
**Phone: (713) 230-0515**  
**FAX: (713) 230-0537**

**CERTIFICATE OF ANALYSIS**

**Job Number: L9910.222A**



**SAYBOLT**

**PRODUCT:** Unknown  
**SAMPLE MARKED:** Oil WP-A8  
**SUBMITTED BY:** RMT Inc., Chicago, Illinois  
**RECEIPT DATE:** October 23, 1999  
**ANALYSIS DATE:** October 25, 1999

<u>RESULTS OF ANALYSIS:</u>	<u>UNITS</u>	<u>TEST RESULTS</u>	<u>METHODS</u>
Surface Tension	dynes/cm	23	ASTM D-1331A
Interfacial Tension	dynes/cm	15	ASTM D-971
Viscosity @ 100°F	cSt	10.33	ASTM D-445
API Gravity @ 60°F		0.9545	ASTM D-4052

*Victor Farlane*

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 Pasadena, Texas



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# **Appendix B**

## **Free Product "True Thickness"**

### **Calculations, API Excel Spreadsheet**

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**Brooks-Corey LNAPL Distribution Worksheet****Enter Data in Yellow Region - Use Consistent Length Units****Monitoring Well Thickness** $b_0 = 2.350$  (length)**Soil Characteristic**

$n = 0.400$  porosity  
 $\lambda = 1.680$  pore size dist. Index  
 $\Psi_{baw} = 0.070$  displacement pressure head (length)  
 $S_{wr} = 0.100$  irreducible water saturation  
 $S_{ors} = 0.080$  residual LNAPL saturation (saturated)  
 $S_{orv} = 0.040$  residual LNAPL saturation (vadose)  
 $S_{or} = 0.080$  resid. LNAPL sat. (rel. perm. calc.)  
 $Z_{orv} = 0.000$  elev. vadose zone residual (length)  
 $Z_{ors} = 0.000$  elev. saturated zone residual (length)

**Fluid Characteristics:**

$\rho_o = 0.910$  LNAPL density (g/cm<sup>3</sup>)  
 $\sigma_{aw} = 65.000$  air/water surface tension (dyne/cm)  
 $\sigma_{ow} = 12.000$  LNAPL/water surface tension (dyne/cm)  
 $\sigma_{ao} = 21.000$  air/LNAPL surface tension (dyne/cm)

**Copy data for Work Chart**

$b_0 = 2.350$  monitoring well thickness in computation  
 $D_o = 0.762$  formation free-product volume (length)  
 $S_o = 0.810$  effective LNAPL layer saturation  
 $k_{ro} = 0.658$  effective LNAPL layer rel. permeability

$\varepsilon = 4.160$   
 $Z_{ao} = 0.212$   
 $Z_{ow} = -2.139$   
 $Z_r = 0.721$   
 $\Psi_{bao} = 0.025$   
 $\Psi_{bow} = 0.144$   
 $\Delta\Psi = 0.119$   
 $Z_{ao} + \Psi_{bao} = 0.236$   
 $Z_{ow} + \Psi_{bow} = -1.995$

**van Genuchten Parameters**

$M = 0.733$   
 $N = 3.745$   
 $\alpha = 10.089$   
 $\alpha_{ao} = 28.418$   
 $\alpha_{ow} = 4.919$

**Computation Work Area:**

	Scale	Elevation	$S_w$	$S_t$	$S_o$	$k_{ro}$	k-integral
$Z_{ors} - \Delta H$		-2.245	1.000	1.000	0.000		
$Z_{ors}$		-1.995	1.000	1.000	0.000		
$Z_{ors}$		-1.995	0.920	1.000	0.080		
$\Psi_{bow} + Z_{ow}$	0.000	-1.995	0.920	1.000	0.080	0.000	0.000
	0.025	-1.939	0.572	1.000	0.428	0.108	0.003
	0.050	-1.883	0.412	1.000	0.588	0.275	0.014
	0.075	-1.828	0.324	1.000	0.676	0.400	0.032
	0.100	-1.772	0.270	1.000	0.730	0.487	0.057
	0.125	-1.716	0.234	1.000	0.768	0.548	0.086
	0.150	-1.660	0.209	1.000	0.791	0.592	0.118
	0.175	-1.604	0.190	1.000	0.810	0.625	0.152
	0.200	-1.549	0.176	1.000	0.824	0.650	0.187
	0.225	-1.493	0.166	1.000	0.834	0.670	0.224
	0.250	-1.437	0.157	1.000	0.843	0.686	0.262
	0.275	-1.381	0.150	1.000	0.850	0.699	0.301
	0.300	-1.326	0.145	1.000	0.855	0.709	0.340
	0.325	-1.270	0.140	1.000	0.860	0.718	0.380
	0.350	-1.214	0.136	1.000	0.864	0.726	0.420
	0.375	-1.158	0.133	1.000	0.867	0.732	0.461
	0.400	-1.102	0.130	1.000	0.870	0.738	0.502
	0.425	-1.047	0.127	1.000	0.873	0.742	0.543
	0.450	-0.991	0.125	1.000	0.875	0.747	0.585
	0.475	-0.935	0.123	1.000	0.877	0.750	0.626
	0.500	-0.879	0.121	1.000	0.879	0.753	0.668
	0.525	-0.823	0.120	1.000	0.880	0.756	0.710
	0.550	-0.768	0.119	1.000	0.881	0.759	0.753
	0.575	-0.712	0.117	1.000	0.883	0.761	0.795
	0.600	-0.656	0.116	1.000	0.884	0.763	0.837

	0.625	-0.600	0.115	1.000	0.885	0.765	0.880
	0.650	-0.545	0.114	1.000	0.886	0.767	0.923
	0.675	-0.489	0.114	1.000	0.886	0.768	0.966
	0.700	-0.433	0.113	1.000	0.887	0.770	1.009
	0.725	-0.377	0.112	1.000	0.888	0.771	1.051
	0.750	-0.321	0.112	1.000	0.888	0.772	1.095
	0.775	-0.266	0.111	1.000	0.889	0.773	1.138
	0.800	-0.210	0.110	1.000	0.890	0.774	1.181
	0.825	-0.154	0.110	1.000	0.890	0.775	1.224
	0.850	-0.098	0.109	1.000	0.891	0.776	1.267
	0.875	-0.043	0.109	1.000	0.891	0.777	1.311
	0.900	0.013	0.109	1.000	0.891	0.778	1.354
	0.925	0.069	0.108	1.000	0.892	0.778	1.397
	0.950	0.125	0.108	1.000	0.892	0.779	1.441
	0.975	0.181	0.108	1.000	0.892	0.780	1.484
$\psi_{bao} + z_{ao}$	1.000	0.236	0.107	1.000	0.893	0.780	1.528
	0.100	0.285	0.107	0.280	0.173	0.000	1.547
	0.200	0.333	0.107	0.200	0.093	0.000	1.547
	0.300	0.382	0.107	0.174	0.067	0.000	1.547
	0.400	0.430	0.106	0.162	0.056	0.000	1.547
	0.500	0.478	0.106	0.156	0.050	0.000	1.547
	0.600	0.527	0.106	0.152	0.046	0.000	1.547
	0.700	0.575	0.106	0.149	0.044	0.000	1.547
	0.800	0.624	0.106	0.148	0.042	0.000	1.547
	0.900	0.672	0.106	0.146	0.041	0.000	1.547
$z_r$	1.000	0.721	0.105	0.145	0.040	0.000	1.547
	0.100	0.721	0.105	0.145	0.040		
	0.200	0.721	0.105	0.145	0.040		
	0.300	0.721	0.105	0.145	0.040		
	0.400	0.721	0.105	0.145	0.040		
	0.500	0.721	0.105	0.145	0.040	A =	1.029
	0.600	0.721	0.105	0.145	0.040		
	0.700	0.721	0.105	0.145	0.040		
	0.800	0.721	0.105	0.145	0.040		
	0.900	0.721	0.105	0.145	0.040		
$z_{orv}$	1.000	0.721	0.105	0.145	0.040	$\alpha =$	-0.250
		0.721	0.105	0.105	0.000	$\chi =$	0.178
	0.100	0.746	0.105	0.105	0.000	$\beta =$	0.917
	0.200	0.771	0.105	0.105	0.000		
	0.300	0.796	0.105	0.105	0.000		
	0.400	0.821	0.105	0.105	0.000		
	0.500	0.846	0.105	0.105	0.000		
	0.600	0.871	0.105	0.105	0.000		
	0.700	0.896	0.105	0.105	0.000		
	0.800	0.921	0.105	0.105	0.000		
	0.900	0.946	0.105	0.105	0.000		
$z_{orv} + \Delta H$	1.000	0.971	0.105	0.105	0.000		

# **Data Sheet for van Genuchten Model of LNAPL Distribution and Permeability**

Basic data comes from the Brooks-Corey Worksheet

EFR21

<i>van Genuchten Parameters</i>		$b_o =$	2.350	(length)
$M =$	0.733	$S_{wr} =$	0.100	
$N =$	3.745	$S_{ors} =$	0.080	
$\alpha =$	10.089	$S_{orv} =$	0.040	
$\alpha_{ao} =$	28.418	$Z_{orv} =$	0.000	elev. vadose zone residual (length)
$\alpha_{ow} =$	4.919	$Z_{ors} =$	0.000	elev. saturated zone residual (length)
		$S_m =$	0.080	minimum liquid sat. (rel. perm. calc.)
		$Z_{ao} =$	0.212	
		$Z_{ow} =$	-2.139	
		$Z_{max} =$	0.714	maximum free-product elevation

## **Effective LNAPL Saturation and Relative Permeability**

$D_o =$	0.779
$S_o =$	0.829
$k_{ro} =$	0.866

## Appendix C: Spreadsheet Calculations of LNAPL Distribution

A spreadsheet has been developed to perform many of the calculations presented in Sections 3.5 and 3.8. This MS Excel spreadsheet (workbook) titled *LNAPL Distribution.xls* is available for download from the web address [www.api.org/ehs/fpr/tools.htm](http://www.api.org/ehs/fpr/tools.htm). It may be used to calculate many of the significant parameters that are used in design and analysis of free-product recovery (FPR) systems, including the effective LNAPL-layer saturation ( $\bar{S}_o$ ) and effective LNAPL-layer relative permeability ( $\bar{k}_{ro}$ ) as a function of monitoring well LNAPL-layer thickness ( $b_o$ ). In addition, the parameters  $\alpha$  and  $\beta$  that are used to calculate LNAPL recovery in the methods presented in this report may also be calculated using the spreadsheet. Application and use of this spreadsheet are described in this appendix.

The spreadsheet (workbook) contains four worksheets. The first worksheet is for data entry. Consistent length units should be used (usually meters or feet). An example is shown in Figure C.1 (the computation area of the worksheet is not shown). On the left of the worksheet are the cells for entering monitoring well LNAPL thickness, Brooks and Corey soil characteristic parameters, and fluid parameters. With a color monitor, this section of the worksheet is colored yellow. On the right of the worksheet are the corresponding values for the various parameters that were discussed in Section 3.5. In particular, the values shown in the section colored green include the monitoring well LNAPL thickness, the formation free-product volume, and the calculated effective LNAPL-layer saturation and relative permeability. Data from this section may be copied to the second worksheet for use in calculation of the parameters  $\alpha$  and  $\beta$ . If a value of  $b_o$  less than the LNAPL entry head is entered on the left, then a value equal to the entry head is used in the calculations and shown on the right (the LNAPL entry head is labeled  $\Delta\Psi$  on the worksheet). For the example shown the LNAPL entry head is 0.061 meters. However, values of  $b_o$  less than  $\Delta\Psi$  are used on the van Genuchten worksheet because the van Genuchten capillary pressure model has a zero entry head. The van Genuchten parameter values corresponding to the Brooks and Corey parameter values that were entered are also shown to the far right on the worksheet. Refer to Appendix E for guidance on selecting appropriate values for  $S_{ors}$  and  $S_{orv}$ .

All workbook cells except for those used in data entry are protected.

KJC (8/14/88)

### Brooks-Corey LNAPL Distribution Worksheet

**Enter data in yellow regions only. Constants are pre-filled.**

Monitoring Well Thickness		
L <sub>1</sub>	1.220	(length)

Soil Characteristics		
n	0.419	porosity
A <sub>s</sub>	0.585	pore size dist. index
h <sub>wp</sub>	0.183	displacement pressure head (length)
S <sub>wp</sub>	0.129	irreducible water saturation
S <sub>wp</sub>	0.000	residual LNAPL saturation (saturated)
S <sub>wp</sub>	0.000	residual LNAPL saturation (vadose)
S <sub>wp</sub>	0.000	resid. LNAPL sat. (rel. perm. calc.)
Z <sub>wp</sub>	0.000	elev. vadose zone residual (length)
Z <sub>wp</sub>	0.000	elev. saturated zone residual (length)

LNAPL Characteristics		
ρ <sub>LNAPL</sub>	0.710	LNAPL density (g/cm <sup>3</sup> )
σ <sub>aw</sub>	65.000	air/water surface tension (dyne/cm)
σ <sub>aw</sub>	28.000	LNAPL/water surface tension (dyne/cm)
σ <sub>aw</sub>	25.000	air/LNAPL surface tension (dyne/cm)

Monitoring Well Thickness in Computation		
L <sub>1</sub>	1.220	monitoring well thickness in computation
L <sub>1</sub>	0.112	formation free-product volume (length)
L <sub>1</sub>	0.000	effective LNAPL layer saturation
L <sub>1</sub>	0.000	effective LNAPL layer rel. permeability

**Figure C.1 Brooks and Corey Data Entry Worksheet**

The second worksheet, shown in Figure C.2, is used for estimating the (set of)  $\alpha$  and  $\beta$  values that are used in equation (3.5.25). Data ( $b_0$ ,  $D_0$ ,  $\bar{S}_0$ , and  $\bar{k}_{r0}$  values) are entered (copied from the first or third worksheet) in the section labeled "Enter data here." Up to 15 data sets may be used. The data must be copied and pasted using the "Edit - Paste Special - Values" sequence. (Alternatively, after the data have been copied from the first or third worksheet one may press "Alt-E-S-V" and then "Enter.") As data are entered, the graph is automatically updated. One may also enter a brief title such as the soil texture. The second part of the work area is for fitting  $\alpha$  and  $\beta$  values to different segments of the data curve. For each segment, initial and final values of  $b_0$  and  $D_0$  are entered. The corresponding segment is shown as a dashed line on the graph. Up to three segments may be used. The example shown in Figure C.2 has only one segment with an initial ( $b_0$ ,  $D_0$ ) point (0.230, 0.000) and final point (2.000, 0.573). The worksheet calculates the corresponding  $\alpha$  and  $\beta$  values, where  $\alpha$  has the same length units selected for the first worksheet. An example graph with three segments is shown in Figure 3.5.5.

The third worksheet, as shown in Figure C.3, provides more detailed information on the van Genuchten parameters, including the formation product thickness, effective saturation and relative permeability values calculated using the van Genuchten model for use with the second worksheet.





In equation (3.3.2),  $i$  can be either  $w$ ,  $a$  or  $o$ , standing for water, air and LNAPL, respectively. The fact that all of the pore space is filled means that the sum of the fluid saturation values must equal unity.

$$S_w + S_a + S_o = 1 \quad (3.3.3)$$

The fluid saturation for any phase can range from 0 to 1.

**Table 3.3.2 Average Porosity (Standard Deviation)  
Values Based on Soil Texture**

Soil Type	Porosity ( $n$ )
Clay	0.38 (0.09)
Clay Loam	0.41 (0.09)
Loam	0.43 (0.10)
Loamy Sand	0.41 (0.09)
Silt	0.46 (0.11)
Silt Loam	0.45 (0.08)
Silty Clay	0.36 (0.07)
Silty Clay Loam	0.43 (0.07)
Sand	0.43 (0.06)
Sandy Clay	0.38 (0.05)
Sandy Clay Loam	0.39 (0.07)
Sandy Loam	0.41 (0.09)

(Source: Carsel and Parrish, 1988)

### 3.4 Capillary Pressure Relationships

When more than one fluid is present within the void space of a porous medium, then an interface exists separating the fluid phases. Molecules located near the interface have a greater energy than molecules of the same fluid located within the bulk volume due to adhesive forces between molecules. The excess energy associated with the interface results in an *interfacial tension* ( $\sigma_{ow}$ ) between different fluids and *surface tension* between a liquid and its vapor ( $\sigma_{ao}$ ).

(published by state by the Natural Resource Conservation Service, formerly the Soil Conservation Service) generally contain soil data for the predominant soil series within a state. A total of 42 books representing 42 states were used to develop the database. They used a multiple regression equation developed by Rawls and Brakensiek (1985) to estimate the retention parameters for the Brooks and Corey model, and estimated the corresponding van Genuchten model parameters from these using the asymptotic equations (3.4.6). Table 3.4.2 shows the mean and standard deviation Brooks and Corey model parameters determined from their study. For different soil texture classes, this table provides guidance to representative magnitudes of the respective parameters and their relative variability.

**Table 3.4.2** Descriptive Statistics from Carsel and Parrish (1988) Data Set

Tabulated Values: Mean (Standard Deviation)

Soil Type	Residual Saturation, $S_{wr}$	Bubbling Pressure Head, $\Psi_b$ (m)	Pore Size Distribution Index, $\lambda$
Clay	0.18 (0.089)	1.25 (1.88)	0.09 (0.09)
Clay loam	0.23 (0.024)	0.53 (0.42)	0.31 (0.09)
Loam	0.18 (0.030)	0.28 (0.16)	0.56 (0.11)
Loamy sand	0.14 (0.037)	0.081 (0.028)	1.28 (0.27)
Silt	0.074 (0.022)	0.62 (0.27)	0.37 (0.05)
Silty loam	0.15 (0.033)	0.50 (0.30)	0.41 (0.12)
Silty clay	0.19 (0.064)	2.0 (2.0)	0.09 (0.06)
Silty clay loam	0.21 (0.021)	1.0 (0.6)	0.23 (0.06)
Sand	0.10 (0.023)	0.069 (0.014)	1.68 (0.29)
Sandy clay	0.26 (0.034)	0.37 (0.23)	0.23 (0.19)
Sandy clay loam	0.26 (0.015)	0.17 (0.11)	0.48 (0.13)
Sandy loam	0.16 (0.041)	0.13 (0.066)	0.89 (0.17)

\*Carsel and Parrish (1988) report mean and standard deviation of van Genuchten's 'a' parameter. Using Eq. (3.4.6) and a first-order expansion, the standard deviation of  $\Psi_b$  is approximated by  $\sigma_{\Psi_b} \approx \frac{\sigma_a}{a^2}$ .

# **Appendix C**

## **LNAPL Volume Calculations**

### **Intergraph Siteworks Model**

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## APPENDIX C

### FREE PRODUCT (LNAPL) VOLUME CALCULATIONS

#### Purpose:

The purpose of the free product volume calculation was to determine the volume of LNAPL (light nonaqueous-phase liquid) that exists in the soil beneath the L.E. Carpenter site in Wharton, New Jersey.

#### Methodology:

The first step of the free product volume calculation was to determine the "true thickness" of free product (volume LNAPL per unit area of soil) using the American Petroleum Institute (API) Excel spreadsheet model (Charbeneau et al., 1999). "True thickness" values were calculated based on measured thickness of free product in 68 monitoring wells at the site. The "true thickness" values of free product were then plotted on a digitized map of the site at the location of each monitoring well or EFR well. The distribution of "true" LNAPL thickness values across the entire area of free product was then evaluated by interpolating between the 68 known points, to derive a grid of LNAPL thickness over the site.

Intergraph's design software "Siteworks" (Intergraph, 1993) was utilized to generate and compare a digital terrain model (3-dimensional surface model) of LNAPL thickness. The lower surface was set equal to zero, and the upper surface was set equal to the "true thickness" (volume per limit area) of LNAPL. The two surfaces, the top of the LNAPL layer and the base (zero) were evaluated on a triangular grid utilizing "Siteworks," to determine the volume of LNAPL over the entire free product area of the site.

#### Results:

The results of the LNAPL volume calculations were as follows:

Base Surface: Set equal to zero (base of LNAPL)

Design Surface: (File J:/3868.21/surf1.dwg) Set equal to thickness of LNAPL

Cut	0 cu ft
Fill	5859 cu ft
Net	5859 cu ft

The "cut" volume is zero, since it assumes a flat surface for the bottom of the LNAPL layer.

The "fill" volume represents the LNAPL volume.

The "net" volume is identical to the fill volume, as the "cut" volume is zero.

The LNAPL volume was calculated to be 5859 cu ft (43,825 gallons). To account for uncertainty in measurements and calculations, this number is rounded to 44,000 gallons.

### **Attachments:**

1. DTM of LNAPL volume generated by Selectcad, showing triangulation between known points
2. Printed report of calculated volumes

### **References:**

Charbeneau, R., R. Johns, L. Lake, M. Adams III, 1999. Free-product recovery of hydrocarbon liquids. American Petroleum Institute (API) Publication No. 4682.

Intergraph. 1993. Draft Intergraph siteworks reference guide. Huntsville, Alabama: Intergraph. December 1993.

